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The study of specific ionic interactions are facilitated by the study of heats of mixing of aqueous electrolytes. Much work has been done with systems at 25°C, but very little work has been done at higher temperatures. In addition, the vast majority of work in this type study has been done with common anion mixings. In order to gain knowledge in the field of solute-solvent interactions a study of common cation interactions at elevated temperatures is considered necessary.

The systems studied were KCl-KBr-H_2O, KCl-KF-H_2O, KCl-$KC_2H_3O_2$-H_2O, and KF-$KC_2H_3O_2$-H_2O at 1.0 molal and constant ionic strength. Temperatures studied were 40°, 60° and 80°C. A new adiabatic microcalorimeter was used in the work.

All of the systems studied showed little or no temperature dependence. This result tends to add validity to the numerous results by other authors who state that the heat of mixing is mainly influenced by interactions occurring at the interface of the primary and secondary hydration spheres of the ions in aqueous solutions.

Several thermodynamic functions are calculated or estimated for the electrolyte solutions as a function of temperature, using the heat of mixing data.

THERMODYNAMICS OF AQUEOUS ELECTROLYTES
TEMPERATURE DEPENDENCE OF THE HEATS OF MIXING OF ANIONS

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In today's changing world of fresh water limitations, the fields of desalination and water pollution are consuming millions of dollars to study the effects of ions and molecules in solution. In the years to come many millions of dollars more will be spent in light of the public awareness of the limitations within our environmental system.

The study of ions and molecules in solution is not new, however. As early as the late nineteenth century Arrhenius[1] established the nature of ionic solutions by postulating positive and negatively charged species in aqueous solution.

It was quickly discovered that there was a difference in the behavior of ions and molecules, depending on the solvent surrounding them. From this noticable difference, theories of why ions and molecules behaved differently in different solvents began to emerge. Since water is by far the most abundant solvent, it is of no suprise that over the early part of the twentieth century many theories concerning the effects of water on ions were published.

Water, although probably the most widely studied solvent, is probably the least understood. This, in part, accounts for the limitations in any theory yet published on the effects of ions in aqueous solution.

One of the most popular methods of studying aqueous

electrolytes is with the use of thermodynamics. This present study is no exception. It is hoped that this work contributes a little more knowledge to the overall understanding of ions in aqueous solution.

DOCUMENTATION OF PREVIOUS WORK

The area of electrolyte chemistry, and particularly aqueous electrolyte theory has entwined its roots in the very foundations of so-called modern chemistry. A brief look into the past of this field of chemistry is a must for a total appreciation of current research in this area. In any active field of research, disagreements in theory occur. This is another good reason to study the history of a field of science.

In 1887 Van't Hoff[2] first applied thermodynamics to solutions in a systematic manner. His theory, although valid only at infinite dilution, paved the way for an understanding of solutions. To account for the ionic character of some solutions, he proposed

$$PV = iRT \qquad \text{(Eq. 1)}$$

where: i= the number of times the osmotic pressure of a given salt solution is greater than the equimolar solution of sugar. P = the pressure, V = the volume, and T = the temperature.

About the same time Arrhenius[3] expanded upon Van't Hoff's theory by proposing a relationship between osmotic pressure and the electrical properties of a solution. He stated that deviations from Van't Hoff's theory were due to those salts which conduct electrical current. Futhermore, these "electrolytes" undergo, in solution, spontaneous dissociation into positive and negative charged part-molecules or ions. Arrhenius also postulated that the molecular conductivity of a solution was a measure of

the concentration of ions, and the degree of electrical dissociation, or the activity coefficient, α , was given by the ratio of the molecular conductivity at the given dilution, to the molecular conductivity at infinite dilution, when all the molecules were regarded as being dissociated into ions.

Sutherland[4] and Noyes[5] both studied ionization of electrolytes and its relationship with viscosity and the laws of ionization for binary electrolytes.

A major breakthrough in aqueous electrolyte theory came from Bjerrum[6]. He first proposed that the typical strong electrolytes are completely dissociated in dilute aqueous solutions. The deviations of such solutions, from ideality, are due to the electrostatic field of force from the ionic charges. In a later publication[7], he defined Φ, the osmotic coefficient, as

$$1-\phi = \frac{\mu_I^{el}}{\nu m R T} \frac{1000}{M_I} \qquad \text{(Eq. 2)}$$

where: μ_I^{el} = electrostatic interaction, and ν = the number of ions.

Van Laar[8] also postulated, several years before Bjerrum's publication, the importance of electrostatic forces in characterizing the behavior of ionic solutions. Around this time Hertz[9] and Ghosh[10] attempted to give the effects of interionic attraction mathmatical expressions, but both gave only qualitative answers.

S.R. Milner[11], around the same time, attempted to calculate the effect of the interionic forces on the thermodynamic properties of solutions. The fundamental principles of the treatment were

unexceptional, but, owing to the great mathmatical difficulty of the problem, he was unable to obtain any explicit formula. However, the results of his approximate computation may be described by stating that for small concentrations of a symmetrical electrolyte of valence type (z, -z) the osmotic coefficient, g, behaves approximately according to the formula

$$1-g = \alpha z^3 C^{\frac{1}{2}} \qquad \text{(Eq. 3)}$$

where C = the volume concentration, and α = a constant depending on the temperature and dielectric constant of the solvent. He also assumed that every positive ion repels every other positive ion, and attracts every negative ion, with a force q^2/r^2, where r is the distance between the pair of ions considered, and q is the ionic charge.

In 1901 G.N. Lewis[12] proposed several new concepts. One of these was the mean activity, defined as

$$a_{\pm} = (a_+ a_-)^{\frac{1}{2}} \qquad \text{(Eq. 4)}$$

and $a_2 = a_+ a_-$. Since a_+ does not always equal a_-,

$$a_{\pm} = a_2^{\frac{1}{2}} \qquad \text{(Eq. 5)}$$

From this equation Lewis and Randall[13] proposed to define activity coefficient as

$$\gamma = \frac{a_{\pm}}{m(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}} \qquad \text{(Eq. 6)}$$

where ν_i = the number of ions of charge i, and m = the molality.

Closely aligned to the activity coefficient, Lewis proposed the concept of ionic strength, I, where

$$I = \tfrac{1}{2}\Sigma mz^2 \qquad \text{(Eq.7)}$$

The activity coefficient is a function of ionic strength, and varies with varying ionic strength.

Other contributors to early theories of electrolytes include Noyes[14], Ostwald[15], and Harned[16]. Harned also proposed an equation for the activity coefficient of uni-univalent strong electrolytes. He labeled the activity coefficient by F_a and defined it as

$$F_a = \alpha c - \beta c^m \qquad \text{(Eq. 8)}$$

where c = the concentration, and α, β, and m are empirical constants. Two years later, Harned and Brumbaugh[17] derived an equation for mixed 1:1 electrolytes.

$$\text{Log } F_a' = \alpha' c_1 - \beta' \mu^{m'} + \alpha''(\mu - c_1) + f'\frac{(\mu - c_1)}{c_1} \qquad \text{(Eq. 9)}$$

where c_1 = the concentration of 1 electrolyte in solution and μ = the ionic strength, and α', β', α'', and f' are empirical constants.

J.N. Brønsted[18] gave consideration to the attraction of ions in solution, and came up with the principle of specific interaction of ions. In a dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of their own sign. Mathematically, he expressed this as

$$\frac{f_x(A_1B)}{f_x(A_2B)} = F(A_1, A_2) \qquad \text{(Eq. 10)}$$

$$\frac{f_y(A_1B)}{f_y(A_2B)} = F(A_1, A_2, y) \qquad \text{(Eq. 11)}$$

where x = an arbitrary cation, y = an arbitrary anion, A_1B = a compound with a common ion, f = the activity coefficient, and

F = an indeterminate function. Therefore, he states, the activity coefficient of an ion is a function of the nature of the ion itself, the solvent containing it, and the action upon it of ions of opposite charge. However, Harned[19] states that common anions can be assumed to posses the same activity, but in their mixtures the activity coefficient of the constituent cations are assumed to vary. The activity coefficient of other cations introduced in small amounts are also assumed to vary from one solution to another.

To further complicate matters, Lewis and Randall[20] assumed that all activity coefficients, at constant total concentration, depend only upon their own nature, and not upon the nature of the solutions containing them. This is termed the "principle of independent activity coefficients."

Brønsted[21] continued to state that only ions of unlike sign approach each other closely enough to produce these specific effects. This area of ion-ion interaction has been called the Interionic-attraction Theory. Other workers in this area included Randall and Young[22], who used EMF to varify the Interionic-attraction Theory, and E. Hückel[23].

However, the front runners in the field of ion-ion interactions at this time were P. Debye and E. Hückel[24]. In 1923 they sucessfully applied mathematics to the problem of ion-ion interaction, and obtained the following equation:

$$\nabla \cdot \nabla \Psi_j^o = 4\pi/D \sum_{i=1}^{j} n_i e_i \exp\left(-\Psi_j^o e_i/kT\right) \qquad \text{(Eq. 12)}$$

where Ψ = the electrical potential (undisturbed), and ∇ = the differential operators, D = the dielectric constant, n = the ionic concentration, and e = the charge on the ion.

The two assumptions of Debye and Hückle were to apply Boltzmann formula to a set of conditions to which it is not strictly applicable, and to combine this with the Poisson equation to form the basis of their treatment. Secondly, they assumed that the mutual electrostatic potential energy of two ions at their closest distance of approach, a, is small compared to their mean thermal energy of translation. The first assumption is equivalent to assuming that the potential of a given ion due to all the remaining ions is directly proportional to the charge of the given ion.

They also proposed an equation for the mean activity coefficient. In its original form it is

$$\ln \gamma_{\pm} = -1/\nu \sum_{1}^{p} \nu_j z_j^2 \left(\frac{\pi N \varepsilon^6}{1000(kDT)^3} \right) \sqrt{\Gamma} \qquad \text{(Eq. 13)}$$

where Γ = the ional concentration, or $d_o \sum_{1}^{s} m_i z_i^2$. This equation, now called the Limiting Law for Activity Coefficients, is expressed more simply as

$$\ln \gamma_{\pm} = -A_{\gamma} |z_+ z_-| I^{\frac{1}{2}} \qquad \text{(Eq. 14)}$$

where A_{γ} = the Debye-Hückel coefficient, which is a function of the charges considered in (Eq. 13). The advantage of this equation is that it can be used for both mixed and single electrolytes.

Debye and Hückel also proposed an equation for the osmotic

coefficient, using the same assumptions as previously stated.

$$1 - \phi = 0.374\, I^{\frac{1}{2}} \frac{\sum_i N_i z_i^2}{\sum_i N_i} \frac{N_{H_2O} + \sum_i N_i}{N_{H_2O} V_{H_2O} + \sum_i N_i V^i} \frac{\sum_i N_i}{-\log(1 - \sum_i N_i)} \sigma\left(\frac{a}{3.08} I^{\frac{1}{2}}\right) \qquad \text{(Eq. 15)}$$

where N = Avogadro's number, and σ = a geometric factor, and a = the closest distance of approach of 2 ions.

Guggenheim[25] took the best from Brønsted's theory and from Debye and Hückel's theory to propose his Variant Theory. In this, he defines the mean activity coefficient as:

$$\log \gamma_{\pm} = -0.50 \frac{z_+ |z_-| I^{\frac{1}{2}}}{1 + \frac{a}{3.08} I^{\frac{1}{2}}} + BI \qquad \text{(Eq. 16)}$$

where B and a are adjustable parameters. For a 1:1 solution a = 3.08 and B = 0. B is explained as an adjustable constant for ionic interactions, or deviations from the Debye-Hückel limiting term.

For mixed electrolytes with the same valence type, he ignores triplet interactions and arrived at the following equations.

$$\log \gamma_{\pm} = -0.50 \frac{z_+ |z_-| I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \frac{c q_+ q_-}{q_+ + q_-} \left(\sum_x \lambda_{r,x'} X_{x'} + \sum_r \lambda_{r',x} X_{r'}\right) \qquad \text{(Eq. 17)}$$

where X = mole fraction, λ = the interaction coefficient, or

$$\lambda = \frac{\sqrt{RX}}{RT \ln 10} \qquad \text{(Eq. 18)}$$

and q_i = the number of + or - ions per molecule. For osmotic coefficients, he arrived at the following:

$$1 - \phi = 0.374\, z_+ |z_-| I^{\frac{1}{2}} \sigma\left(\frac{a}{3.08} I^{\frac{1}{2}}\right) \qquad \text{(Eq. 19)}$$

About 1915, H.S. Harned[26] began using electrochemical cells

as a method for studying activity and activity coefficients. Cells of the type,

$$H_2|HX_{(m_1)}\ MX_{(m_2)}|AgX\text{-}Ag \qquad \text{(Eq. 20)}$$

were especially good for these type studies. With the ionic strength kept constant, the general equation for the above cell is,

$$E^{o\prime} = E^{o} - \frac{2RT}{F} \ln \gamma_{\pm} \qquad \text{(Eq. 21)}$$

where $E^{o\prime} = E^{o}$ when $I = 0$.

For the activity coefficient of one solution in another solution, the empirical relationship, known as Harned's rule is:

$$\log \gamma_1 = \log \gamma_{(0)1} + \alpha_{12} m_1 \qquad \text{(Eq. 22)}$$

$$= \log \gamma_{1(0)} - \alpha_{12} m_2 \qquad \text{(Eq. 23)}$$

where γ_1 = the activity coefficient of electrolyte I in the mixture, and $\gamma_{(0)1}$ = the activity coefficient of electrolyte I at zero concentration in the presence of electrolyte 2 at a given ionic strength. $\gamma_{1(0)}$ = the activity coefficient of electrolyte I in a pure solution of I, and α_{12} = the slope of the line obtained for Log γ_1 versus m. Additional parameters which can be added to Harned's rule include a $-B_i m_i^2$ term for better fit.

Several years later Guggenheim[27], using Brønsted's theories, developed his equations for γ_1 and γ_2 for a system MY and NX in water.

$$\log \gamma_1 = -A_\gamma \frac{m^{\frac{1}{2}}}{1+m^{\frac{1}{2}}} + m_1 B_{mx} + \tfrac{1}{2} m_2 (B_{nx} + B_{my}) \qquad \text{(Eq. 24)}$$

and,

$$\log \gamma_2 = -A_\gamma \frac{m^{\frac{1}{2}}}{1+m^{\frac{1}{2}}} + m_2 B_{mx} + \tfrac{1}{2} m_1 (B_{nx} + B_{my}) \qquad \text{(Eq. 25)}$$

where B_{ij} = the specific ion interaction constants. These equations relate to Harned's equations as follows:

$$\alpha_{12} = B_{ny} - \tfrac{1}{2}(B_{my} + B_{nx}) \qquad \text{(Eq. 26)}$$

and,

$$\alpha_{21} = B_{mx} - \tfrac{1}{2}(B_{my} + B_{nx}) \,, \qquad \text{(Eq. 27)}$$

also,

$$\alpha_{12} - \alpha_{21} = B_{mx} - B_{ny} \qquad \text{(Eq. 28)}$$

$$= \frac{2(\phi_2 - \phi_1)}{2.303\ m} \qquad \text{(Eq. 29)}$$

and,

$$\alpha_{12} + \alpha_{21} = B_{mx} + B_{ny} - B_{my} - B_{nx} \,. \qquad \text{(Eq. 30)}$$

Where m = n, or x = y,

$$\alpha_{12} = -\alpha_{21} \qquad \text{(Eq. 31)}$$

$$= \frac{\phi_2 - \phi_1}{2.303\ m} \qquad \text{(Eq. 32)}$$

$$= \tfrac{1}{2}(B_{ny} - B_{mx}) \qquad \text{(Eq. 33)}$$

During this same time period other methods for activity coefficient studies were used. These include isopiestic methods, notably by Bausfield[28], and by Sinclair[29]. Sinclair's method was by use of a desiccator in which several solutions were maintained at a constant temperature. The vapor pressures were brought into equilibrium with a reference solution which has an accurately known vapor pressure. By analysis of the vapor pressure of these solutions after equilibrium has been reached, and by the use of the Gibbs-Duhem equation, the activity coef-

ficient of each can be calculated, since the vapor pressure of pure water is also measured. Work by Owen and Cook[29] also belongs here.

Lewis and Randall[30] and Randall and Young[31] provided another equation for the activity coefficient. This equation allows the calculation of the activity coefficient at any given temperature if it is known at some other temperature.

$$\log \gamma'' = \log \gamma' - \frac{1000}{\nu M_1} \int_0^x \left(\frac{1}{m}\right) dx \qquad \text{(Eq. 34)}$$

where γ'' = the activity coefficient at a reference temperature T'', and γ' = the measured activity coefficient at T'. Where ν = the number of ions, M_1 = the molecular weight, m = molality, and x = a function of heat content.

Several years later, G. Scatchard, et. al.,[32] began publishing results of work using the freezing point measurements of various solutions to determine the activity coefficient. The results were then interpreted as modifications to Brønsted's theory by the addition of terms to include triplet and pairwise interactions.

Based on the above foundation using single electrolyte theory, a new look at the mathematical theory was attempted by Joseph Mayer.[33] Using statistical mechanical techniques, he derived several equations.

$$\bar{F}_{2\,(c,P,T)} = \bar{F}^{\circ}_{2\,(P,T)} + \nu RT \,\mathrm{Ln}(\gamma_{\pm}\, C_{\pm}) \qquad \text{(Eq. 35)}$$

where

$$C_{\pm} = c\left[\nu_+^{\nu_+}\, \nu_-^{\nu_-}\right]^{1/\nu} \qquad \text{(Eq. 36)}$$

and $\bar{F}^{\circ}_2$ = the standard partial molal free energy, and $\bar{F}_2$ = the free energy of the solution. For activity coefficients, he proposed,

$$\log \gamma_{\pm} = - \sum_{s=1}^{s=\sigma} \sum_{r=1}^{r=\sigma} x_s x_r (Q_{sr} - K_{sr}) \qquad \text{(Eq. 37)}$$

where σ = the number of chemical species, Q_{sr} = a function of S, and K_{sr} = a function of S.

These equations prove to be independent of the Debye-Hückel equation, but provide an equal result at infinite dilution. The basic differences between the two theories is that Mayer's ionic solution theory is derived from the theory of the virial coefficients of imperfect gases and is independent of the Debye-Hückel theory and free from the somewhat dubious physical and mathmatical inconsistencies of the earlier theory.

Mayer also presented his theories of solute-solvent interaction. Based on molecular modeling, he presented his "primitive model" for ion-solvent interaction. The solvent is represented as an ideal structureless dielectric whose properties are independent of the electric field strength, and the ions are represented as hard spheres with the same dielectric constant as the solvent and with the charge in an arbitrary but fixed spherical distribution within each ion. He formulated his statistical mechanical model by using cluster integrals. In this, he considered only ++, +-, and -- interactions as the main potentials of force at work in a solution of less than 1 molar and increasing as a function of increasing approach.

An extention of Mayer's work was attempted by J.C. Poirier[34]. Since Mayer derived equations for the mean activity coefficient, which is usually not measured, Poirier extended these calculations to obtain generally measured thermodynamic quantities.

$$\ln \gamma = \ln \gamma_{\pm} - P_{osm}[\bar{V}_2^{\circ}/\nu RT - \beta_1] \qquad \text{(Eq. 38)}$$

where γ = the stoichiometric mean ionic molal activity coefficient, and P_{osm} = the osmotic pressure, $\bar{V}_2^{\circ}$ = the partial molal volume at infinite dilution, and β_1 = the coefficient of isothermal compressibility.

Poirier also derived equations for partial molal volume, apparent molal volume, relative partial molal heat content and relative apparent molal heat content. The equations he obtained give good agreement with the experimental results, up to approximately 0.4 molal for 1:1 electrolytes.

In the early fifties, H.A.C. McKay[35], proposed an equation to deal with deviations from Harned's rule.

$$\log (\gamma_1/\gamma_1^{\circ}) = -\alpha_{12} m_2 + \beta m_2^2 \qquad \text{(Eq. 39)}$$

and,

$$\alpha_{21} m_1 = [\log (\gamma_2^{\circ}/\gamma_1^{\circ})]_{m=m_2}^{m=m} + m_2[\alpha_{12}]_{m=m_2}^{m=m} + \int_{m_2}^{m} \alpha_{12}\, dm \qquad \text{(Eq. 40)}$$

He also expressed the excess free energy of mixing in terms of the activity coefficients and osmotic coefficients of the solution.

$$\Delta_m G^E = G_m^E - (G_1^E + G_2^E) \qquad \text{(Eq. 41)}$$

$$= 2RT\,(m_2 \ln (\gamma_1/\gamma_1^{\circ}) + m_3 \ln (\gamma_2/\gamma_2^{\circ} - m\phi + m_1\phi_1^{\circ} + m_2\phi_2^{\circ}) \qquad \text{(Eq. 42)}$$

or,

$$\Delta_m G^E = -(\alpha_{12} + \alpha_{21})\, m_1 m_2\, RT \qquad \text{(Eq. 43)}$$

where

$$\ln (\gamma_i/\gamma_i^{\circ}) = -\alpha_{ij} m_j \qquad \text{(Eq. 44)}$$

Harned[36] used the cell,

$$H_2 \mid HCl_{(m_1)}; NaCl_{(m_2)} \mid AgCl\text{-}Ag \qquad \text{(Eq. 45)}$$

where the activity coefficient (γ_1) of HCl was determined. The equation used was,

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12} m_2 \qquad \text{(Eq. 24)}$$

where $\log \gamma_{1(0)}$ = the activity coefficient of pure HCl ($m_1 = m$), and m_2 = the concentration of NaCl.

By using the method of McKay[35], Harned computed α_{21} in the equation

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21} m_1 \qquad \text{(Eq. 46)}$$

where γ_2 = the activity coefficient of NaCl in the final solution, and $\gamma_{2(0)}$ = the activity coefficient of NaCl when $m_2 = m$. For two uni-univalent electrolytes in solution, McKay's equation states that

$$\alpha_{21} m_1 = \left[\log \gamma_{2(0)} / \log \gamma_{1(0)} \right]_{m=m_2}^{m=m} + m_2 \left[\alpha_{12} \right]_{m=m_2}^{m=m} + \int_{m_2}^{m_1} \alpha_{12} dm \qquad \text{(Eq. 47)}$$

but when m_1 approaches m.

$$\alpha_{21(m)} = \log(\gamma_{2(0)}/\gamma_{1(0)}) + \int_0^m \alpha_{12} dm \qquad \text{(Eq. 48)}$$

$$\alpha_{21(0)} = \frac{d \log(\gamma_{2(0)}/\gamma_{1(0)})}{dm} + \frac{m d\alpha_{12}}{dm} + \alpha_{12} \qquad \text{(Eq. 49)}$$

At this same time Harned gave equations for the excess free energy of mixing and the excess heat of mixing.

$$\Delta_m G^E = -2.303\, RT m_1 m_2 \left[(\alpha_{12(0)} + \alpha_{21(0)}) + 2\beta_{21} m_2 \right] \qquad \text{(Eq. 50)}$$

and

$$\Delta_m H^E = 2.303\, RT^2 m_1 m_2 d\left[(\alpha_{12(0)} + \alpha_{21(0)}) + 2\beta_{21} m_2 \right] \qquad \text{(Eq. 51)}$$

For the system HCl-NaCl-H_2O, Harned proposed, using γ_1 = HCl,

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12(0)} m_2 \qquad \text{(Eq. 22)}$$

but,

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21(0)} - \beta_{21} m_{12} \qquad \text{(Eq. 53)}$$

Equation (53) uses the additional parameter to account for the non-linearity of this system.

Harold L. Friedman[37] expanded upon Mayer's[33] work and found an inconsistancy with Brønsted's principle of specific ion interaction. Using the equation

$$\Delta_m G^{Ex}_{(y,I)} = I^2 RTy(1-y)[g_0 + g_1 Y + g_2 Y^2 + \cdots] \qquad \text{(Eq. 54)}$$

where $Y = 1-2y$, and g_p $(p=0,1,2,\cdots)$ = pairwise like charge interactions measurements, and y = mole fraction. He found that $\Delta_m G^{Ex}/I^2$ does not vanish as I approaches zero, as is expected on the basis of Brønsted's principle. He looked at both symmetrical and non-symmetrical mixtures in this respect. Another equation related to $\Delta_m G^{Ex}$ is $\Delta_m H^{Ex}$. Friedman gives this equation for the excess heat of mixing.

$$\Delta_m H^{Ex}_{(y)} = I^2 y(1-y) RT \sum h_p Y^p \qquad \text{(Eq. 55)}$$

where

$$h_p = -T[\partial g_p / \partial T] \qquad \text{(Eq. 56)}$$

Experimental confirmation to Friedman's theoretical calculations are exhibited by Wood, et. al.[38]. They showed that the quantity RTh_0 (a measure of the magnitude of ionic interaction) shows no general trend with concentration.

In the case of Scatchard and Prentiss[40], their equation for $\Delta_m G^{Ex}$ is

$$\Delta_m G^{Ex}(cal/Kg) = x(1-x) I^2 RT g_0 \qquad \text{(Eq. 57)}$$

where,

$$g_0 = AI + BI^{3/2} + \cdots \qquad \text{(Eq. 58)}$$

and A and B are functions of triplet ionic interactions. Wood, et. al.[39] have used this calculation for their experimental data and found g_0 to be in error by two to five times the possible experimental error. In this the Wood school of thought which contradicts the Brønsted principle , and the Scatchard school, which upholds the principle, continue to maintain their individual lines of thought.

In any study of ionic interactions, the investigation of the solute-solvent role is critical. Many authors have commented on the role that a solvent plays in ion-ion interactions[41-49]. The Gibbs-Duhem equation is the foundation for describing most solute-solvent relationships.

$$X_A d\mu_A + X_B d\mu_B = 0 \qquad \text{(Eq. 59)}$$

where μ = the chemical potential, and A = the solvent, and B = the solute. Also,

$$d(\ln a_B) = -\frac{X_A}{X_B} d(\ln a_A) \qquad \text{(Eq. 60)}$$

where a = the activity, and X = the mole fraction. In a multi-component solution, the Gibbs-Duhem equation becomes,

$$(X_1 d\ln a_1 + X_2 d\ln a_2 + X_3 d\ln a_3 + \cdots = 0)_{P,T} \qquad \text{(Eq. 61)}$$

The structuring of water around individual ions has been recognized for many years as a factor in the properties of ions in solution. Much active work still continues in this field, as no conclusive results have proven any one theory on solvent-ion structuring.

G.W. Stewart[50] noticed, in 1943, that there was a striking correspondence between the rate of variation of the partial molal ionic volume with concentration, and the rate of variation of H_2O structure as seen by x-ray analysis.

Robinson[51] indicated a positive $\bar{s}_1 - \bar{s}_1^\circ$ value as being typical of a structure breaking effect, whereas a negative $\bar{s}_1 - \bar{s}_1^\circ$ value indicates a structure strengthening effect, where s is entropy. A dipole moment is not the main factor determining the thermodynamic properties of these solutions, he noted.

Collie, Hasted, and Ritson[52] postulated that liquid water is considered to be made up of ordered regions of microcrystalline domains whose boundries are in continuous motion. When inorganic ions are added to the water, they are considered to break up the structure to some extent, to increase the boundary area and shorten the relaxation time.

Hückel[53] showed that a variation of dielectric constant would have a significant, if not dominant effect on the properties of concentrated salt solutions. He also discussed the attraction of H_2O molecules to an ion. This attraction occurs as a sheath of several layers of water molecules around the ion.

In 1926 Webb[54] found that the energy changes associated with the solution of ions in various solvents are important in that they permit a calculation of the absolute activities of ions. That is, with reference to a state independent of any solvent.

Bernal and Fowler[55] argued in 1933 that water surrounds ions in solution essentially as a tetrahedral arrangement. If

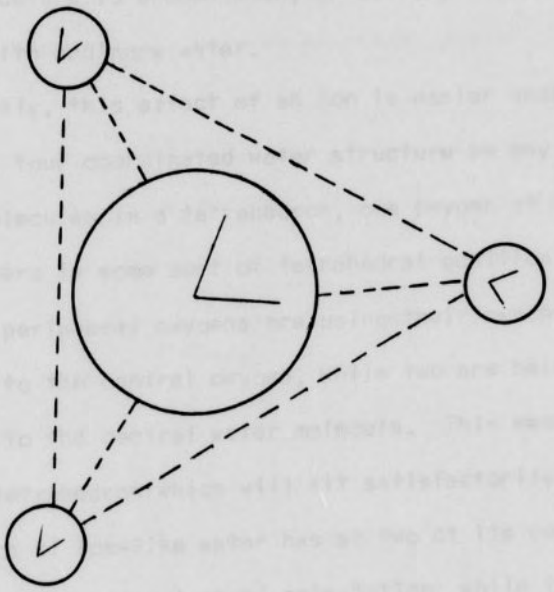
an ion is completely hydrated, it will carry a number of water molecules around it. The maximum hydration will be limited by the number of H_2O molecules which can be packed in mutual contact around the ion. This depends only on the ionic radius. All larger ions (Cl^-, Br^-, and $C_2H_3O_2^-$) have four coordination in water solutions (see figure 1).

Beginning in 1940 Frank[56] found that cations of small radii tend to stabilize the H_2O structure, while large ions have the opposite effect. Frank and Evans[57] made a detailed study of this effect by looking at change of entropy of hydration versus temperature of rare gas atoms and non-polar molecules. When a rare gas atom or non-polar molecule dissolves in water at room temperature, it modifies the water structure in the direction of greater crystallinity. The water, so to speak, builds a microscopic iceberg around it. The extent of this iceberg is greater the larger the foreign atom. This freezing of water produced by the atom causes heat and entropy to be lost beyond what would be otherwise be expected.

In the substitution of an ionic atom or molecule, the charge has a dramatic effect on the system. The ΔH values are seven to ten times as great as those characteristic of non-ionic solutions. However ΔSvalues are in exactly the same range (18 to 40 e.u.) as those for non-polar solutes. This is illustrated by comparing the entropy loss of K^+ and Cl^- (both isoelectronic with argon) to two argon atoms. K^+Cl^- = 25.3 e.u. + 26.6 e.u. = 51.9 e.u. Ar + Ar = 30.2 e.u. + 30.2 e.u. = 60.4 e.u. The effect of the

Tetrahedral Arrangement of Water Around an Ion

Figure I



charges is actually to lessen the entropy loss.

The conclusion is that in an ionic solution there is "too much entropy", just as in the rare gas solution there is "too little entropy". The probable explanation, according to Frank and Evans, is that around the ions, beyond the first saturated region of water molecules, there is a region or belt in which the water structure is broken down, or melted, or depolymerized, as compared with ordinary water.

"Pictorially, this effect of an ion is easier understood. In the normal four coordinated water structure we may think of five water molecules in a tetrahedron, one oxygen at the center, with four others in some sort of tetrahedral position around it. Two of these peripheral oxygens are using their own hydrogens to bind them to the central oxygen, while two are held by hydrogens which belong to the central water molecule. This means that the kind of tetrahedron which will fit satisfactorily into an extended patch of ice-like water has at two of its corners water molecules which have one type of orientation, while the orientation at the other two corners must be different. Assume now that it is desired to fit a positive ion, Na^+, say, into the structure. The most favorable way to do this will be to give it a coordination shell of four water molecules, and let these assume positions around it in which the oxygens are at the corners of a tetrahedron. This is opposed to two water molecules oriented one way, and two oriented opposite, as required for a good fit into an iceberg.

When we include the influence of ionic size, it is clear

that it will be necessary to go out some distance from a positive ion before the water has recovered itself sufficiently to have its characteristic structure and entropy."

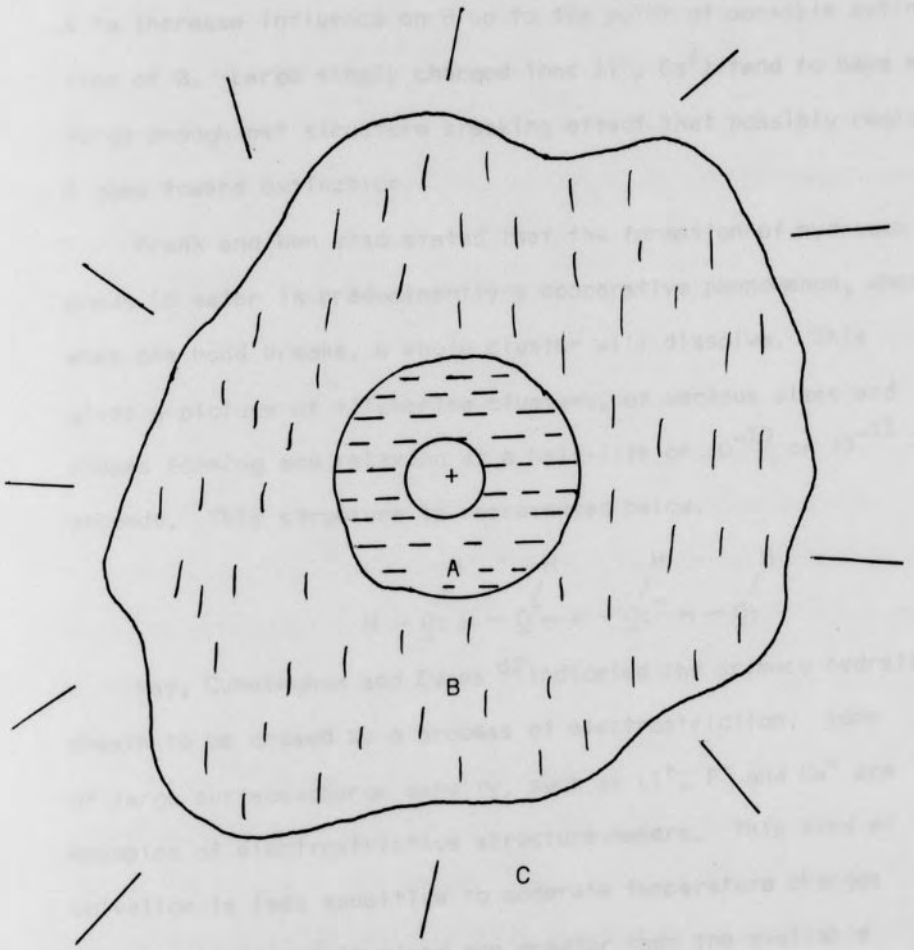
About 1948 through 1949 Collie, Hasted and Ritson[58] published a series of articles in which they looked at dielectric relaxation times and correlated this with the structure breaking phenomena as denoted by Frank and Evans. It was found that for a large structure breaking effect, a large positive change in fluidity should be noted.

Panthaleon, et. al.,[59] showed in 1957, using x-ray diffraction, that the cation (especially for KCl) is surrounded by an octahedral arrangement of water. Haggis, et. al.,[60] also found some ions to contain six to eight coordination of water to cation.

In figure 2 Frank and Wen[61] show pictorially the hydration sphere around a cation. It turns out that in a study of the entropy of hydration, all of the alkali metal cations except Li^+ and Na^+, and all of the halides except F^-, lose too little entropy when dissolved from the gaseous state to infinite dilution. In figure 2 the cause of the structure breaking region is presumably the approximate balance in region B between two competing orienting influences which act on any given water molecule. One of these is the normal structural orienting influence of neighboring water molecules. The other is the orienting influence upon the dipole of the spherically symmetrical ionic field. The latter influence predominates in region A, and the former in region C, and it is not implausible that between A and C

Water Structure Around an Ion

Figure 2

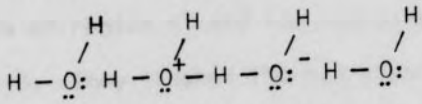


A = Region of immobilized water
B = Region of structure breaking
C = Normally structured water

there should be a region of finite width in which significantly more orientational disorder should exist than in either A or C, or in unperturbed water.

Small cations with single or double charges causes region A to increase influence on B up to the point of possible extinction of B. Large singly charged ions (I^-, Cs^+) tend to have a large enough net structure breaking effect that possibly region A goes toward extinction.

Frank and Wen also stated that the formation of hydrogen bonds in water is predominantly a cooperative phenomenon, where, when one bond breaks, a whole cluster will dissolve. This gives a picture of flickering clusters, of various sizes and shapes forming and relaxing at a half-life of 10^{-10} or 10^{-11} seconds. This structure is represented below.



Kay, Cunningham and Evans [62] indicated the primary hydration sheath to be caused by a process of electrostriction. Ions of large surface-charge density, such as Li^+, F^- and Ca^+ are examples of electrostrictive structure-makers. This kind of solvation is less sensitive to moderate temperature changes because the forces involved are greater than the available thermal forces.

There are two other types of ionic structure: those with small surface-charge densities, structure breakers, such as Cs^+ or I^- ions; and those with very small surface-charge densities

but with surfaces of inert alkyl or aryl groups. These are called hydrophobic structure makers since water molecules surrounds them with a greater degree of hydration, due to hydrogen bonding, than bulk water. Examples are Bu_4N^+ and Ph_4B^- ions.

As temperature increases the amount of structured water decreases, and the structure breaking power of these ions is decreased. Just the reverse is the case with the large ions with hydrophobic surfaces (such as $C_2H_3O_2^-$). These ions have a structure making ability, and an aqueous mobility deficiency which disappears as increased thermal motion disrupts the added structure.

Kay and Evans[63], using conductance experiments, found agreement with the Frank and Wen model. In general, high charge and small size or low charge and large hydrophobic surface area increase the size of region A, and low charge and large size increases region B. They likened the hydration to a cage around the large inert portion of large molecules.

Gurney[64] showed that ionic mobility studies and their temperature coefficients tend to confirm the structured effect of the water-ion interaction. Brandy[65] has shown in direct x-ray studies of the structure of the immediate environment of such a large multicharged ion as Er^{+3}, that a highly ordered structure is maintained even beyond the region of primary hydration, its similarity to the structure of ice being considerably more marked than when pure water and ice are compared.

Frank[66] looks at the structure of water, using Raman spectroscopy and X-ray scatter. He concludes that cold water seems to consist of hydrogen-bonded, four coordinated, framework regions, with interstitial monomers occupying some fraction of the cavities formed by the framework. This framework appears to be regular at colder temperatures and becomes more random as the water gets warmer.

Somoilov[67] stated that the hydration of ions in solution can be divided into two regions. The first region (close hydration) is comprised by the interaction of the ions with the water molecules which form the immediate surroundings of the ions in the solution, and the second region (distant hydration), by the interaction with more distant water molecules. The distant hydration depends mainly on a polarization of the surrounding volume of water by the action of the ionic field, and it always corresponds with the considerable energy decrease which accompanies the transfer of the ions into the solution. The close hydration describes the action of the ions on the thermal, and principally the translational, motion of the adjacent water molecules of the solution. The so-called kinetic properties of solutions are chiefly dependent on this close hydration.

Vdovenko, et. al.,[68] looked at the displacement of the structural equilibrium between the icelike and close-packed structures (the two-structure model) under the influence of the electrostatic field of the ion is examined on a theoretical basis. They conclude that in the electrostatic field due to an ion, the structural

equilibrium in water is displaced in favor of the iceberg structure.

Luck and Diiter[69] examined the structure of water using near-infrared spectroscopy. They showed that some ions produce an increase in intensity in the wavelength region of free OH^- (structure breakers) and some ions produce a decrease of intensity in the region of the free OH^- vibration (structure makers).

By neutron inelastic scattering techniques, Leung and Safford[70] showed the existence of primary hydration spheres or layers. Also, for the ions Cs^+, K^+, and Na^+ there were found to be primary ion-water complexes which were specific for a given salt. With increased temperature, water-water coordinations were rapidly disrupted, and the number of primary hydration waters increased.

Tikhomirov[71] argues that strong primary H_2O interactions can lead to the polarization of H_2O bonds and to a strengthening of bonds beyond the primary layer, which would tend to decrease the reorientational freedom. The relative influence of the reduction of the number of bonds in the intermediate region and of this cooperative strengthening of bonds by polarization would affect the average diffusive kinetics, and determine the structure making or breaking influence of the salt.

Endom, et. al.,[72] noted from spin-echo measurements of the self-diffusion coefficients of water molecules in aqueous solutions, that KCl, KBr, KI, CsCl, and CsBr at low temperatures (25°C) show a structure breaking tendency. In contrast, at higher temperatures, they show a structure making tendency.

Y.C. Wu, M.B. Smith and T.F. Young[73] looked at systems

of 1:1 electrolytes in 1 molal solutions. They postulated an equation for the heat of mixing in the following manner:

$$\Delta_m H/x_2x_3 = A + Bx_3 + \cdots \qquad \text{(Eq. 62)}$$

Young, et. al.,[74] had previously shown that most systems could be adequately described with only the A and B constants. It was also pointed out that the heats of mixing of Cl^- and Br^- is nearly the same whether the mixing is done in the presence of Li^+, Na^+, or K^+. The interactions between a pair of the same charge sign are typically affected relatively little by the common ion.

Young, et. al.,[75] derived an equation where:

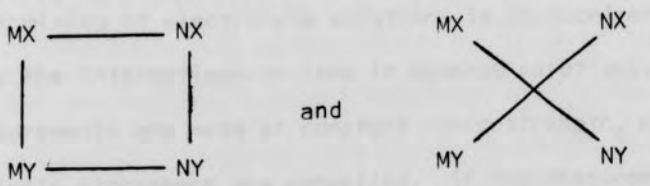
$$\tfrac{1}{2}[(MY + NY) + (MX + NX)] + \tfrac{1}{2}[(MX + MY) + (NX + NY)] + \varepsilon =$$

$$\tfrac{1}{2}[(MX + MY) + (NX + NY)] + \tfrac{1}{2}[(MY + NY) + (MX + NX)] + \varepsilon' \qquad \text{(Eq. 63)}$$

where M and N are different cations of the same charge and $\varepsilon = \varepsilon'$, where

$$\varepsilon = \Delta_m H - \tfrac{1}{2}[\Delta_m H_{mx,nx} + \Delta_m H_{my,ny}] \qquad \text{(Eq. 64)}$$

and X and Y are different anions of the same charge. This equation can be pictorially represented as follows.



where,

$$\tfrac{1}{2}[(MX + NY) + (MX + NX)] + \tfrac{1}{2}[(MX + MY) + (NX + NY)] + \varepsilon =$$

$$\tfrac{1}{2}[(MX + NY) + (MY + NX)] \qquad \text{(Eq. 65)}$$

or, in shorthand notation:

$$\tfrac{1}{2}\left[\square\right] + \varepsilon = \tfrac{1}{2}[\ X \qquad \text{(Eq. 66)}$$

but generally ε is small in relation to experimental error, and is neglected. Therefore,

$$\tfrac{1}{2}\sum\square = \tfrac{1}{2}\sum X \qquad \text{(Eq. 67)}$$

which is called the "cross-square rule" for heats of mixing.

This derivation shows that since Brønsted's principle of Specific Ionic Interaction requires that the heat of a homoionic mixing is zero, or very small, application of the cross-square rule to a system obeying the principle suggests that the heats of cross mixing (at $x_3 = 0.5$) should be equal in magnitude, but of opposite algebraic sign.

The requirement for the Brønsted theory is that as I becomes smaller, $\Delta_m H/I \rightarrow 0$, but in the system LiCl-NaCl, $\Delta_m H$ becomes smaller as I becomes smaller and does not become equal to zero. Smith[76] shows that for the system NaCl-Na_2SO_4 $\Delta_m H/I$ actually increases as I approaches zero. This deviation is also discussed by Stern and Passchier[77].

In 1965, Wood and Smith[78] noted that the measurement of heats of mixing of electrolyte solutions is an excellent way to study the interactions of ions in aqueous solutions. If the measurements are made at constant ionic strength, effects of the ionic atmosphere are cancelled. If the measurements are made with a common ion, the effects of oppositely charged ion pairs cancel. Thus, the pair-wise and triplet interactions of like-charged ions can be conveniently studied.

Free energy measurements, because of the smallness of change,

show no deviation from Brønsted's theory if triplet interactions are included. However, heats of mixing are larger and therefore more capable of showing changes.

Wood extended his measurements to a low enough concentration to detect differences between like-charged pairs and triplets (0.1 molal to 0.5 molal). The results showed that like-charged ions do have specific interactions even at low concentrations. They are larger than triplet interactions and generally smaller than oppositely charged pair interactions.

The two primary results from this work were that ΘTh_0 showed no general trend with concentration, which is contrary to Brønsted's theory, and the work adds further proof to Friedman's postulation that like-charged and triplet interactions are the main contributors to the heats of mixing. The cross square rule was found to hold in these experiments.

Wood and Anderson[79] derived a set of general equations based on Friedman's mixed electrolyte theory. These equations allow prediction of the excess free energy of mixing and relative apparent molal heat content of any multicomponent mixtures of electrolytes of the same charge type, from the knowledge of only the thermodynamic properties of component pure electrolyte solutions and the common ion mixtures.

Since,

$$G^E_{mix} = \sum_{ij} y_{R_i} y_{X_j} G^E_{R_iX_j} + \Delta_m G^E \qquad \text{(Eq. 68)}$$

where G^E_{mix} = the total excess free energy per kilogram of solvent containing R_i cations and X_j anions, $G^E_{R_iX_j}$ = the total excess

free energy per kilogram of solvent of component pure electrolyte R_iX_j, and y = the mole fraction. The value $\Delta_m G^E$ = the total excess free energy per kilogram of solvent of mixing the single component solutions at constant ionic strength.

The equation they derived is defined as:

$$\Delta_m G^E = RTI^2\left[\sum_{h>i} y_{R_h} y_{R_i} y_{X_j} g^{X_j}_{R_h R_i} + \sum_{j>k} y_{X_j} y_{X_k} y_{R_i} g^{R_i}_{X_j X_k}\right] \quad \text{(Eq. 69)}$$

In this case the result is calculated from a weighted average of the interactions of all the cations in the presence of all the anions, and vice versa. The weighting factors are the respective ion mole fractions (y), the interaction parameter ($g^{X_j}_{R_h R_i}$, etc.) which includes both pairwise and triplet interactions. Interactions of three like-charged ions are not included because they contribute only asymmetry to the equations and have been shown experimentally to contribute very little[80].

One can then write,

$$G^E_{mix} = y_{R_i} y_{X_j} G^E_{R_i X_i} + RTI^2\left[\sum_{h>i} y_{R_h} y_{R_i} y_{X_j} g^{X_j}_{R_h, R_i} + \sum_{j>k} y_{X_j} y_{X_k} y_{R_i} g^{R_i}_{X_j, X_k}\right] \quad \text{(Eq. 70)}$$

and,

$$H^E_{mix}/m = \sum y_{R_i} y_{X_j} \phi_L^{R_i X_j} + \frac{RTI^2}{m}\left[\sum_{h>i} y_{R_h} y_{R_i} y_{X_j} h^{X_j}_{R_h, R_i} + \sum_{j>k} y_{X_j} y_{X_k} y_{R_i} h^{R_i}_{X_j, X_k}\right] \quad \text{(Eq. 71)}$$

where $\phi_L^{R_i X_j}$ = the pure component apparent molal heat content. Both equations uses only knowledge of the properties of single electrolyte solutions and common ion mixtures.

Wood and Anderson[81] also showed that for large hydrophobic

structure making ions, the effect of the overlap of the hydration spheres predominate in both the heat of mixing and the heat of dilution, so that the heat of mixing can be predicted.

Anderson and Petree[82] studied the heat of mixing of large tetraalkylammonium cations, Li^+, K^+, H^+, and Na^+ cations from 25°C to 80°C to see if Brønsted's prediction of zero heat of mixing would be met. None of the systems tended toward zero, therefore not supporting this theory.

In the study of anion-common cation mixings, very little work is available in the literature. Wu, et. al[83] found that the heat of mixing of the Cl^- and Br^- ions in the presence of Li^+ (0.81 cal/mole) differs very little from the heat of mixing of these same anions in the presence of the Na^+ ion (0.79 cal/mole). This gives rise to the value of 0.80 cal/mole for the heat of mixing of $Cl^-$and Br^- in an equimolar solution of Li^+ and Na^+ ions. The same approximate value holds in the case of Li^+, Na^+, or K^+ mixings of Cl^- and Br^-. This suggests that the interactions between a pair of the same charge sign are typically affected little by the common ion.

Wood and Anderson [84] noted that up to 1967 the only anion mixings were Cl^-, Br^-, and NO_3^-, which gave only 1 cal/mole for the Cl^--Br^- mixings and 3 cal/mole for halogen-NO_3^- mixings. They decided to study the system Cl^-, Br^-, $C_2H_3O_2^-$, and F^- at 25°C so that mixings could be classified according to both size and structure.

The heats of mixing of the anions in the presence of the

common potassium ion were found to range from +2.38 to -8.58 cal/mole at 1 molal. This appears to be smaller than the cation-common anion heats of mixing (-50 to +30 cal/mole), but when the very small ions, H^+ and Li^+, are left out of the cation comparison, the heats of mixing range from +2 to -12 cal/mole. If the heat of mixing is mainly influenced by the solvent sphere about an ion, it should not be unreasonable to find abnormally high interactions with the H^+ and Li^+ ions. The present results indicate that the anion heats of mixing can certainly be comparable in magnitude with those of the cation heats of mixing.

The results show that the structural classification can be correlated with the sign of the heats of mixing, whereas the size classification can not. Thus, for all common-ion heats of mixing that have been measured, the mixing of two structure breakers or two structure makers give endothermic heats of mixing, while mixing a structure breaker with a structure maker gives an exothermic heat of mixing. The Cl^- and Br^- are structure breakers, while the F^- and $C_2H_3O_2^-$ ions are structure makers.

In the case of the F^- ion, the structure is created by the high electric field while for the $C_2H_3O_2^-$ ion the lack of specific interaction with the methyl group stabilizes a more highly hydrogen-bonded water structure around this part of the molecule. In addition, there is probably a region near the oxygens where the high electric field creates structure.

They concluded from this work that the heat of mixing is mainly influenced by the water structure about the like-charged ions.

EXPERIMENTAL

ANALYSIS AND STANDARDIZATION

Approximately 3.5 liters each of 2-4 molal stock solutions were prepared using Mallinckrodt analytical reagent grade potassium floride, potassium chloride, potassium bomide, and potassium acetate, which were dissolved in distilled water that had been passed through a demineralization column.

The potassium chloride and potassium bromide stock solutions were standardized by precipitation as the respective silver halide using a 0.1 molar silver nitrate solution. The precipitate was dried to constant weight at 110°C. The potassium floride and potassium acetate stock solutions were precipitated as potassium tetraphenylborate using the following procedure as described by Reilley[85]. A 3% solution was prepared from Fisher 99.9% pure sodium tetraphenylborate. This solution was filtered and stored in an amber bottle. From this, a 0.03% wash solution was prepared. Three 0.4 gram samples of the salt solution to be standardized were weighed out, and diluted to a volume of 250 milliliters with deionized water. To this, 5 milliliters of 50% potassium free sodium hydroxide were added, then the solution was heated to boiling. With vigorous stirring, 50-60 milliliters of 3% sodium tetraphenylborate were added dropwise from a buret. The resulting solution was allowed to cool to

room temperature and then filtered through a fine sintered porcelain crucible. The precipitate was washed with several aliquots of approximately 10 milliliter portions of the previously prepared wash liquid. The final wash was with 5-6 portions of approximately 10 milliliters each of deionized water. The crucibles were then dried to constant weight at 110°C.

To insure the accuracy of this method, a triplicate determination was performed on a previously standardized potassium chloride stock solution. The results were then compared to the results obtained from the silver halide determinations. They agreed within 0.1%.

All standardizations of the stock solutions were performed in quadruplicate, and the results of these can be seen in table 1. The solutions were stored in polyethylene bottles. The potassium acetate solution was stored in the coolest place possible, without refrigeration, because of the tendency for bacterial growth in the solution.

From these stock solutions, operational solutions were prepared by direct weight dilution to 1.0 molal. To accomplish this the following dilution formula was used.

$$\frac{\text{Wt. stock}}{\text{Kg. soln.}} = \frac{m}{m_s}\left[\frac{1000}{(m)(MW) + 1000}\right]\left[(m_s)(MW) + 1000\right] \quad \text{(Eq. 72)}$$

where m = the desired concentration, m_s = the molality of stock solution, and MW = the molecular weight of the salt.

Periodic checks were made on the 1.0 molal potassium chloride and potassium bromide solutions by the Fajan's relative

halide method, using approximately 0.1 molar silver nitrate solution[86].

CALORIMETER

An adibatic calorimeter of microdegree sensitivity (5×10^{-6}°C), similar in design to a previously reported calorimeter system[84] was used. The major differences from the previously described calorimeter are: a) the use of a Keithley model 150B Microvolt-Ammeter and model 370 recorder, Fluke model 881A D.C. Differential Voltmeter and a Heathkit Regulated Low Voltage Power Supply, b) one calorimeter per superstructure and c) an increase in vessel and pipet capacity by a factor of 3. The advantage in an increase in size is not in the precision, but in the accuracy of the data obtainable. A schematic diagram of this calorimeter can be seen in figure 3.

The calorimeter consists of three major parts: 1) temperature monitoring, 2) chemical mixing capability, and 3) electrical calibration. The experimental procedure involves comparison of an unknown amount of chemical heat with an accurately known amount of electrical heat input.

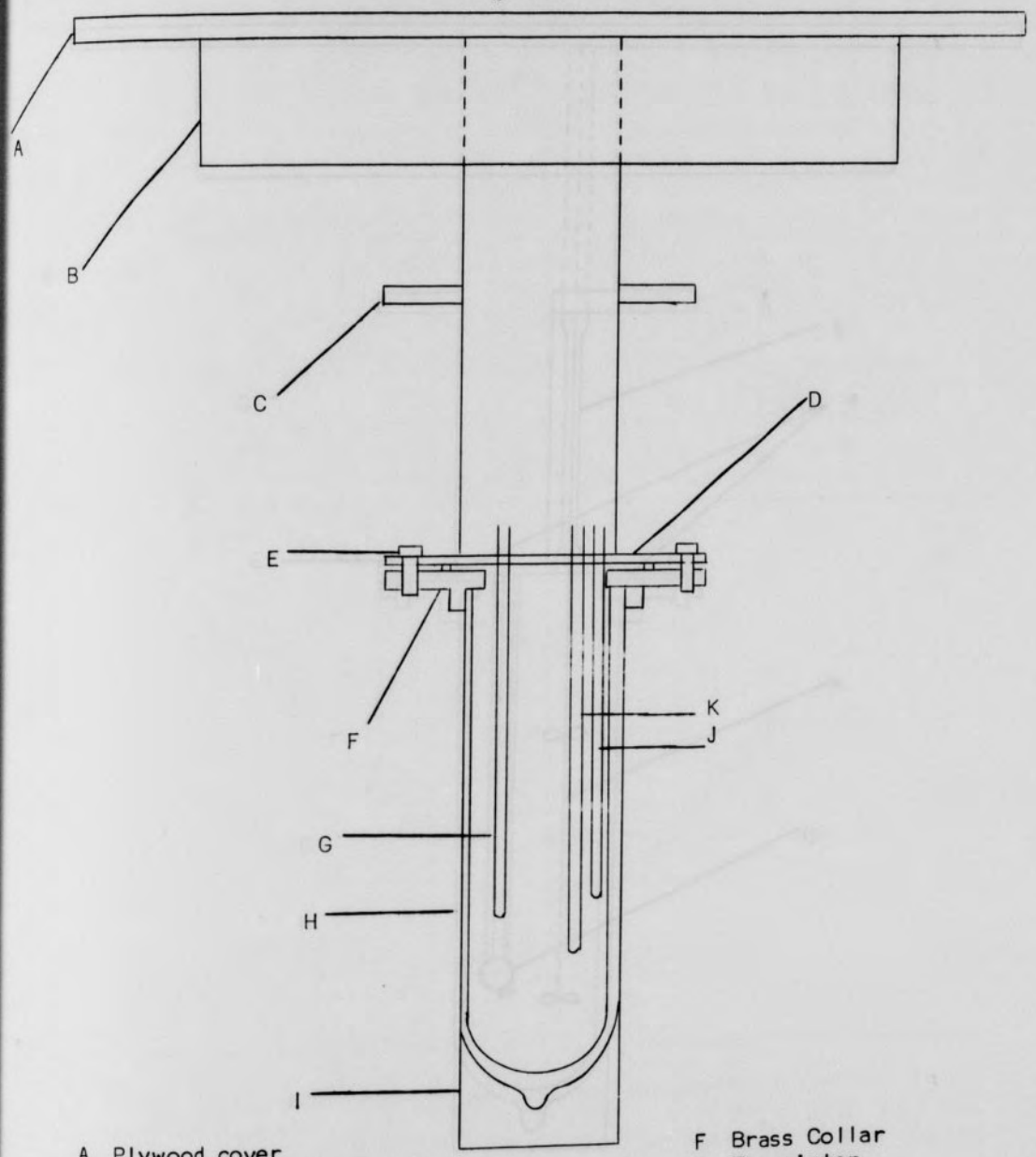
A schematic diagram for the temperature monitoring system can be seen in figure 4. The system is a Wheatstone bridge curcuit in which a 12.5 kilohm thermistor, submerged into the solution, comprises one leg. Where R_1 = 111,111 ohm six dial decade resistor, and R_2 = 11 kilohm two dial decade resistor, R_3 = a 20 kilohm standard resistor, and R_4 = a 12.5 kilohm thermistor, R_2 is adjusted for the desired temperature range used, and remains

TABLE I

Molality of Stock Solutions

Salt Solution	Average Molality
KCl I	3.595 ± .005
KCl II	2.356 ± .001
KBr	3.786 ± .002
KF I	4.050 ± .003
KF II	2.160 ± .002
$KC_2H_3O_2$ I	3.618 ± .005
$KC_2H_3O_2$ II	1.355 ± .002

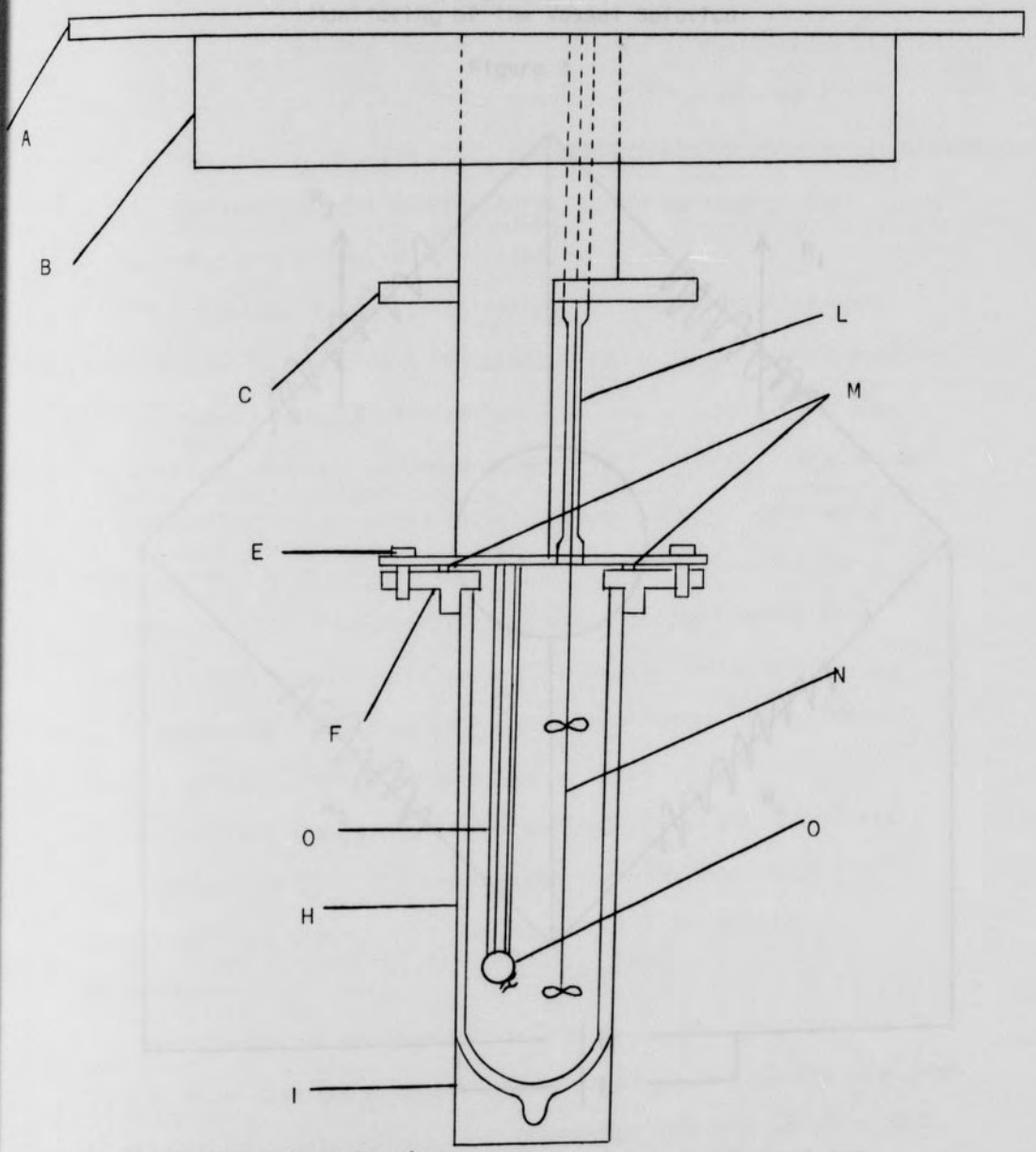
Adibatic Calorimeter
Front
Figure 3



A Plywood cover
B Styrofoam
C 4" x 4" x 1/4" Brass Plate
D Brass Lid
E Brass Screws

F Brass Collar
G Thermistor
H Dewar Flask
I Metal Support
J Calibration Heater
K Rough Heater

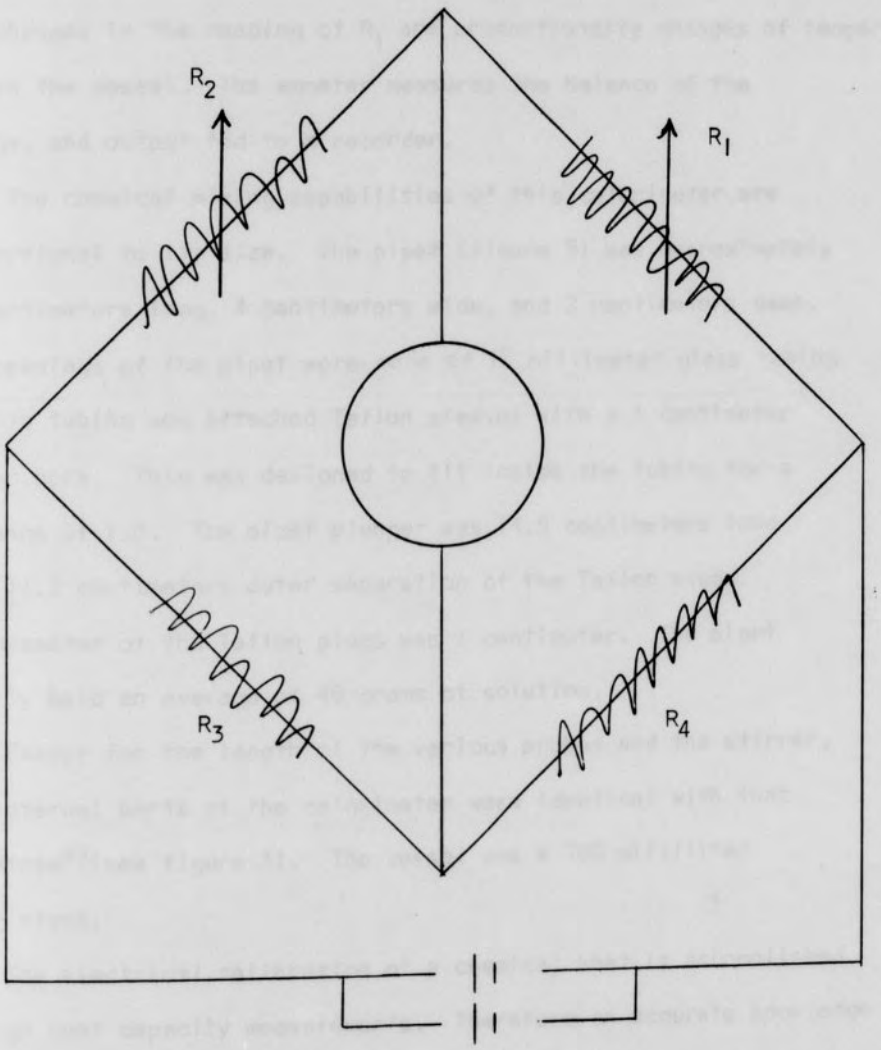
Side View
Figure 3 (continued)



L 5 mm Precision Bore Bearing
M O-rings
N Glass Stirrer
O Teflon Pipet Holder

Wheatstone Bridge Used in Temperature Monitoring of the Vessel Solution

Figure 4



R_1 = 111, 111 ohm six dial decade resistor
R_2 = 11 kilohm two dial decade resistor
R_3 = 20 kilohm standard resistor
R_4 = kilohm thermistor

fixed for that particular temperature. The resistance of the thermistor, R_4 , varies according to changes of temperature within the vessel (see table 2). It is brought into balance by R_1. The changes in the reading of R_1 are proportionally changes of temperature within the vessel. The ammeter measures the balance of the bridge, and output fed to a recorder.

The chemical mixing capabilities of this calorimeter are proportional to its size. The pipet (figure 5) was approximately 11 centimeters long, 4 centimeters wide, and 2 centimeters deep. The openings of the pipet were made of 15 millimeter glass tubing. To this tubing was attached Teflon sleeves with a 1 centimeter center bore. This was designed to fit inside the tubing for a distance of 1.0. The pipet plunger was 14.5 centimeters long with 11.2 centimeters outer separation of the Teflon plugs. The diameter of the Teflon plugs was 1 centimeter. The pipet usually held an average of 40 grams of solution.

Except for the length of the various probes and the stirrer, the internal parts of the calorimeter were identical with that of Petree[87](see figure 3). The vessel was a 700 milliliter dewar flask.

The electrical calibration of a chemical heat is accomplished through heat capacity measurements. Therefore an accurate knowledge of the amount of electrical heat introduced into the solution must be known. A preliminary step to this is the accurate calibration of the small heater. This was accomplished by the following procedure. An SR-1 1000.00 ohm standard resistor[88] was connected

TABLE II

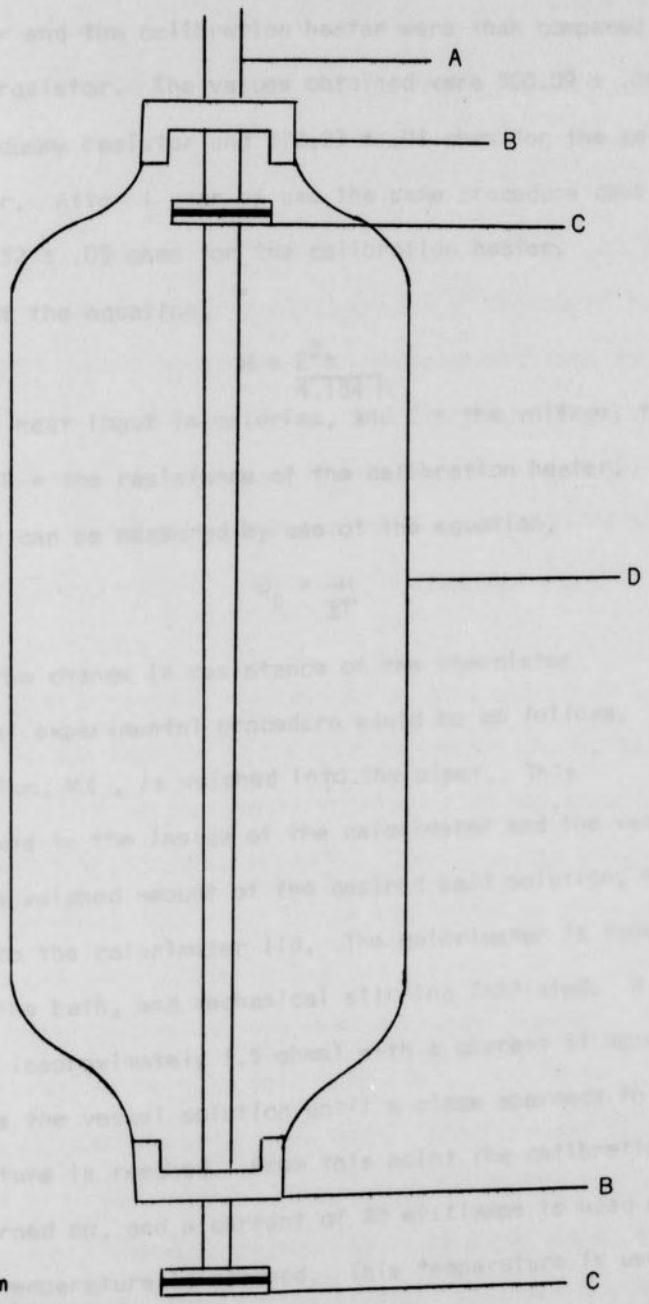
Resistor Settings as a Function of Temperature

Temperature	R_1 (ohms)*	R_2 (kohms)
25°C	19940.0	6.8
40°C	20200.0	5.4
60°C	19600.0	3.2
80°C	18137.0	1.8

* approximate values with water in the vessel

Calorimeter Pipet

Figure 5



A plunger stem
B Teflon sleeve
C Teflon plug
D 15 mm glass tubing blown to size

to the low voltage supply via the differential voltmeter. The dummy resistor and the calibration heater were then compared to the standard resistor. The values obtained were 500.09 ± .08 ohms for the dummy resistor and 512.23 ± .01 ohms for the calibration heater. After 1 year of use the same procedure gave a value of 512.32 ± .05 ohms for the calibration heater.

By use of the equation,

$$H = \frac{E^2 t}{4.184\ R} \qquad \text{(Eq. 73)}$$

where H = the heat input in calories, and E = the voltage, t = the time and R = the resistance of the calibration heater. The heat capacity can be measured by use of the equation,

$$C_p = \frac{-H}{\Delta T} \qquad \text{(Eq. 74)}$$

where ΔT is the change in resistance of the thermistor

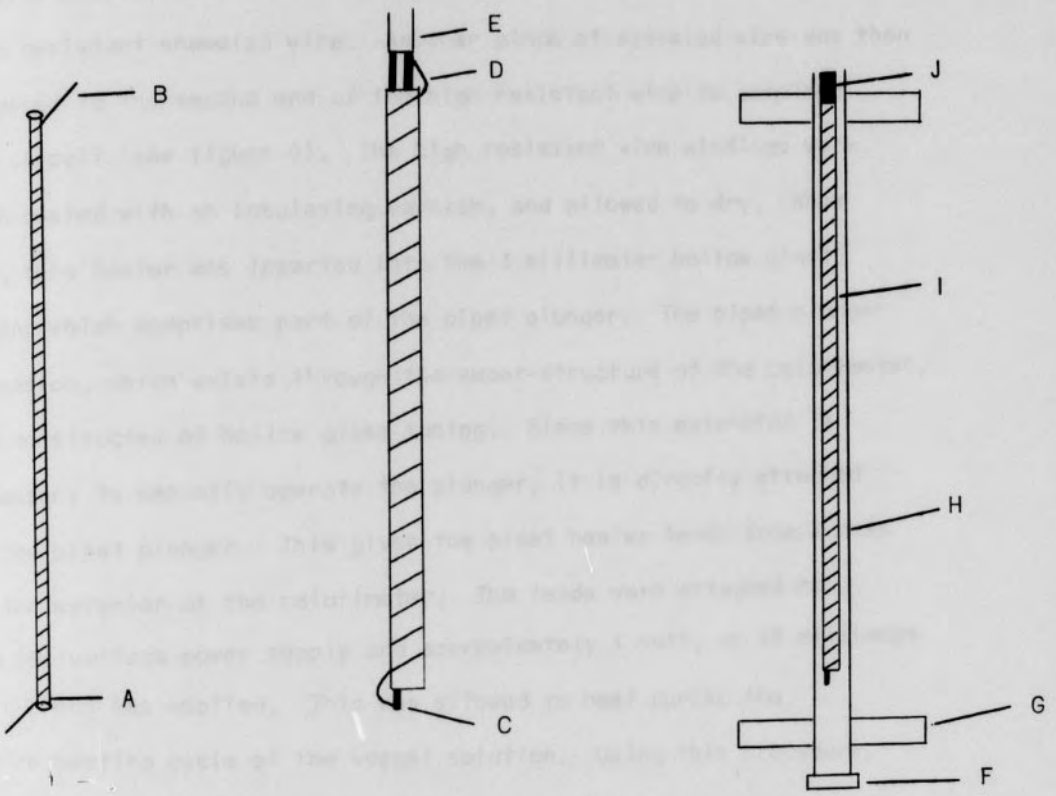
A typical experimental procedure would be as follows. A salt solution, MX , is weighed into the pipet. This is then affixed to the inside of the calorimeter and the vessel, filled with a weighed amount of the desired salt solution, MY , is attached to the calorimeter lid. The calorimeter is then placed into the bath, and mechanical stirring initiated. A rough heater (approximately 1.5 ohms) with a current of approximately 4 amps, heats the vessel solution until a close approach to the bath temperature is reached. From this point the calibration heater is turned on, and a current of 40 milliamps is used until the desired temperature is reached. This temperature is usually when the vessel is a little cooler than the bath. Once equilibrium is reached, the desired straight line has a slope of approximately 0.06 calories per minute, indicating that the vessel is gaining

heat. The pipet is then opened and equilibrium is re-established. The variable resistor, R_1 , is used to bring the bridge back to a balanced state, and the new slope recorded. This change in resistance, ΔR , is directly proportional to ΔT of opening and mixing. From this point, two separate heat capacities are obtained by applying a known voltage for a given time, and noting the displacement of the equilibration slopes with respect to the previously equilibrated position. The average heat capacity is then used with the ΔT obtained for mixing. This gives the quantity, q (mixing) , by the simple relation $q = \Delta C_p \times \Delta R$. The calorimeter is then quickly disassembled and the vessel solution transferred to polyethylene cantainers, taking much care to eliminate evaporation.

Although size presented no problems at 25°C , it soon became apparent that as one went to higher temperatures with the calorimeter system, equilibration of the vessel solution with the unopened pipet solution presented a problem. At 60°C , where one would normally expect from 45 minutes to 1 hour for an equilibration time lag for the smaller calorimeters, this system took as long as 4 hours or more. Since this drastically reduced the number of runs possible per day, it was found necessary to correct this condition. The largest portion of equilibration time comes from the vessel solution equilibrating with the pipet and its contents. Since the pipet solution is much colder, and is not stirred, a method had to be obtained to heat the pipet solution while enclosed in the vessel. This was accomplished by taking 4-5 inches of fine, insulated wire[90] having a resistance of

Pipet Heater Construction

Figure 6



A 70 mm X 1 mm glass tubing
B Evanohm wire
C Soldered joing to 1st lead through 1 mm ID tubing
D Soldered joint to 2nd lead outside of 1 mm ID tubing
E Shrinkable spagetti
F Epoxy bottom plug
G Teflon plug for pipet
H 3 mm ID glass tubing
I Heater
J Shrinkable spagetti

approximately 70-100 ohms. This thin wire was wound on the exterior of a 70 millimeter x 1 millimeter hollow glass tube and soldered to a high resistant enameled wire. Another piece of enameled wire was then soldered to the second end of the high resistant wire to complete the circuit (see figure 6). The high resistant wire windings were then coated with an insulating varnish, and allowed to dry. When dry, this heater was inserted into the 3 millimeter hollow glass tubing which comprises part of the pipet plunger. The pipet plunger extension, which exists through the super-structure of the calorimeter, was constructed of hollow glass tubing. Since this extension is necessary to manually operate the plunger, it is directly attached to the pipet plunger. This gives the pipet heater leads free access to the exterior of the calorimeter. The leads were attached to the low voltage power supply and approximately 1 volt, or 10 milliamps of current was applied. This was allowed to heat during the entire heating cycle of the vessel solution. Using this procedure, the maximum equilibration time obtained at 80° C was 1½ hours. Although some heat is given off to the pipet solution by the heater, probably most of the benefit is from small convection currents set up by the heater. This, in turn, produces a stirring of the pipet solution, carrying heat from the walls of the pipet to the center of the solution.

EXPERIMENTAL PROCEDURE

Since the heat of mixings of anions with a common cation is within the range of 3-40 calories per kilogram of solvent, a calorimeter with a sensitivity in the microdegree range must be

used. This calorimeter had a sensitivity in the order of 10^{-6}°C. Although the calibration of this calorimeter had previously been performed prior to this investigation[91], a check was considered proper. The heat of mixing of NaCl - KCl at 25°C was performed. An average uncorrected RTh_0 of -38.3 calories per kilogram of solvent was obtained. This value compared with the values of -38.5 [92] and -38.3 [93] calories per kilogram of solvent previously reported. Because the general experimental procedure has been described by various authors[94], a detailed treatment will not be given here.

All experiments were performed at a constant total ionic strength of 1.0. Measurements were made in reference to the bath temperature, which was regulated to ±.004°C or less, determined by quartz thermometer[95]. The vessel was loaded with approximately 620 grams of solution MX initially, and the pipet with approximately 40 grams of the solution MY to be mixed. All weights of solutions were adjusted to allow for volume expansion at the more elevated temperatures. After the initial opening, an average mole fraction of 0.07 of the pipet salt MX was obtained, and 0.93 mole fraction of the vessel solution MY. By reusing this solution as the next vessel solution, any desired mole fraction of MX-MY could be obtained. The average fractions investigated were from 0.0-0.4 and 1.0-0.6.

Initially a matched volt-ammeter and recorder was used in recording data. On the 10 microvolt scale the recorder had a sensitivity of 90 divisions per ohm. It was later discovered that by using the 1 volt output on the volt-ammeter to drive a 125 millivolt recorder, the sensitivity could be increased to the

point that at 100 microvolts a response of 360 divisions per ohm was obtained.

TREATMENT OF DATA

The experimental data was fitted, using the method of least squares, to the equation[96],

$$\Delta H_m(\text{cal/kg solvent/molal}) = y(1 - y)I^2[RTh_o + RTh_1(1 - 2y)] \qquad \text{(Eq. 76)}$$

where ΔH_m = the heat of mixing in calories per kilogram of solvent, and y = mole fraction of the salt of the largest formula weight, I = the total ionic strength, R = the universal gas constant, T = Kelvin temperature, h_o = the magnitude of the interaction, and h_1 = the measure of the asymmetry or skew, since y(1 - y) is orthogonal to y(1 - y)(1 - 2y).

An IBM 1401 computer was used to fit the data using a Fortran program (see appendix). Because a successive mixing scheme was used the actual experimental heat observed is the heat difference in the final and initial solutions where,

$$q(\text{experimental}) = q(\text{final}) - q(\text{initial}) \qquad \text{(Eq. 77)}$$

or,

$$q(\text{experimental}) = \Delta_m H(\text{final}) - \Delta_m H(\text{initial}) \qquad \text{(Eq. 78)}$$

upon substitution of equation 76 into equation 78 one obtains,

$$q(\text{experimental}) = RTh_oF1 + RTh_oF2 \qquad \text{(Eq. 79)}$$

where,

$$F1 = (y_F - y_F^2)\,WTSF - (y_I - y_I^2)WTSI \qquad \text{(Eq. 80)}$$

and,

$$F2 = [(y_F - y_F^2) - 2(y_F^2 - y_F^3)]WTSF - [(y_I - y_I^2) - 2(y_I^2 - y_I^3)]WTSI \quad \text{(Eq. 81)}$$

where y_F = the mole fraction, after mixing, of the component with the largest molecular weight, and y_I = the mole fraction, before mixing, of the component with the largest molecular weight, WTSF = the final weight of the solvent, after mixing and WTSI = the initial weight of the solvent, before mixing.

The standard deviation of RTh_o and RTh_I were evaluated using the T-test[97] for significance, at the 95% confidence level. In addition, an F variance test was computed to test for the significance of RTh_I. When h_I was found to be negligible, it was set equal to zero. A copy of the computer program used in this author's work appears in the appendix.

ERRORS

Errors due to concentration, dilution, and neutralization upon mixing any two solutions were less than the experimental uncertainty in all experiments performed (see table 3). All solutions were checked for pH and found to be near 7.0. Preparation of 1.0 molal solutions was accomplished with dilution by direct weight and were accurate to 0.05% or less. The heats of openings were established at each temperature, and corrections were made on the q value obtained. The average heat of opening was between 0.000 and 0.026 ±.008 calories, usually increasing in magnitude with an increase in temperature (see table 4). To further minimize errors in reporting the heat of mixings, all calculations, weights, and measurements were read to 4 significant

figures. When reporting the values of the heats of mixing, the values of RTh_o were reported to 0.1 calorie.

TABLE III

Estimated Heats of Dilution, Considering a Maximum 0.1% Concentration Error With 1.000 Molal Solutions

Salt Solution	Maximum Heat at Dilution (Calories)
$KC_2H_3O_2$	0.3
KBr	0.2
KCl	0.2
KF	0.1

TABLE IV

Heats of Opening at Different Temperatures With Water

Temperature	Heat at Opening (Calories)
25°C	.0039 ± .0018
40°C	.0139 ± .0030
60°C	.0239 ± .0009
80°C	.0255 ± .0085
	.0066 ± .0001*

*New pipet

DISCUSSION

As stated previously, it was the intent of this work to study anion-common cation mixings. The reaction sequence is as follows:

$$MX + MY \rightarrow M^+ + X^- + Y^- \qquad \text{(Eq. 82)}$$

where the initial and final solutions maintain a constant ionic strength. This leads to the situation where the only new interactions present in the final mixture are X^- Y^- type interactions. The other advantage is that a constant ionic atmosphere is maintained at all times.

In this study the heats of mixing $\Delta_m H$ was considered the most accurate method of studying ionic interactions. Since the total heat of mixing is comprised of the ideal and the excess heats of mixing,

$$\Delta_m H = \Delta_m H^i + \Delta_m H^E \qquad \text{(Eq. 83)}$$

and $\Delta_m H^i$ is equal to zero when temperature, pressure and concentration are held constant,

$$\Delta_m H = \Delta_m H^E \qquad \text{(Eq. 84)}$$

The systems $KF-KC_2H_3O_2-H_2O$, $KCl-KBr-H_2O$, $KCl-KF-H_2O$ and $KCl-KC_2H_3O_2-H_2O$ were studied for the effects that temperature had upon the heats of mixing. This work involved reinvestigating the 25°C heat of mixings as well as establishing heat of mixing for these systems at 40°C, 60°C and 80°C. This data is presented in table 5.

SOLUTE-SOLVENT INTERACTIONS

Based on the Frank, Wen and Evans[98] model for an ion in solution, the following interpretations are given to this author's results (see figures 2 and 7).

In the systems KF-$KC_2H_3O_2$-H_2O and KCl-KBr-H_2O, the heats of mixings show no temperature dependence. However, in the systems KCl-KF-H_2O and KCl-$KC_2H_3O_2$-H_2O there is a small temperature dependence, with the heats of mixings going through an apparent minimum in the 40°C - 50°C temperature range. For all four of these systems the temperature dependence is small enough to warrant the conclusion that the types of interactions for these anions are no different than those recorded for the bulk of the cation mixings reported previously by Anderson and Petree[99]. It appears that the water in the region of the structure-making, structure-breaking interface is either thermally stable or very nearly thermally stable for these anions.

From the heats of mixing data one usually can calculate the excess free energy of mixing, $\Delta_m G^E$, at any temperature (T_2) if a reference $\Delta_m G^E$ at any T_1 is known.

$$\Delta_m G^E(t_2) = \Delta_m G^E(t_1) + \Delta_m C_p \Big]_{t_2}^{t_1} \Delta T - \Delta_m S^E(t_1)\Delta T - T_2 \Delta_m C_p \Big]_{t_1}^{t_2} \ln(T_2/T_1) \qquad \text{(Eq. 85)}$$

where

$$\Delta_m C_p = \frac{\Delta_m H(t_2) - \Delta_m H(t_1)}{\Delta T} \qquad \text{(Eq. 86)}$$

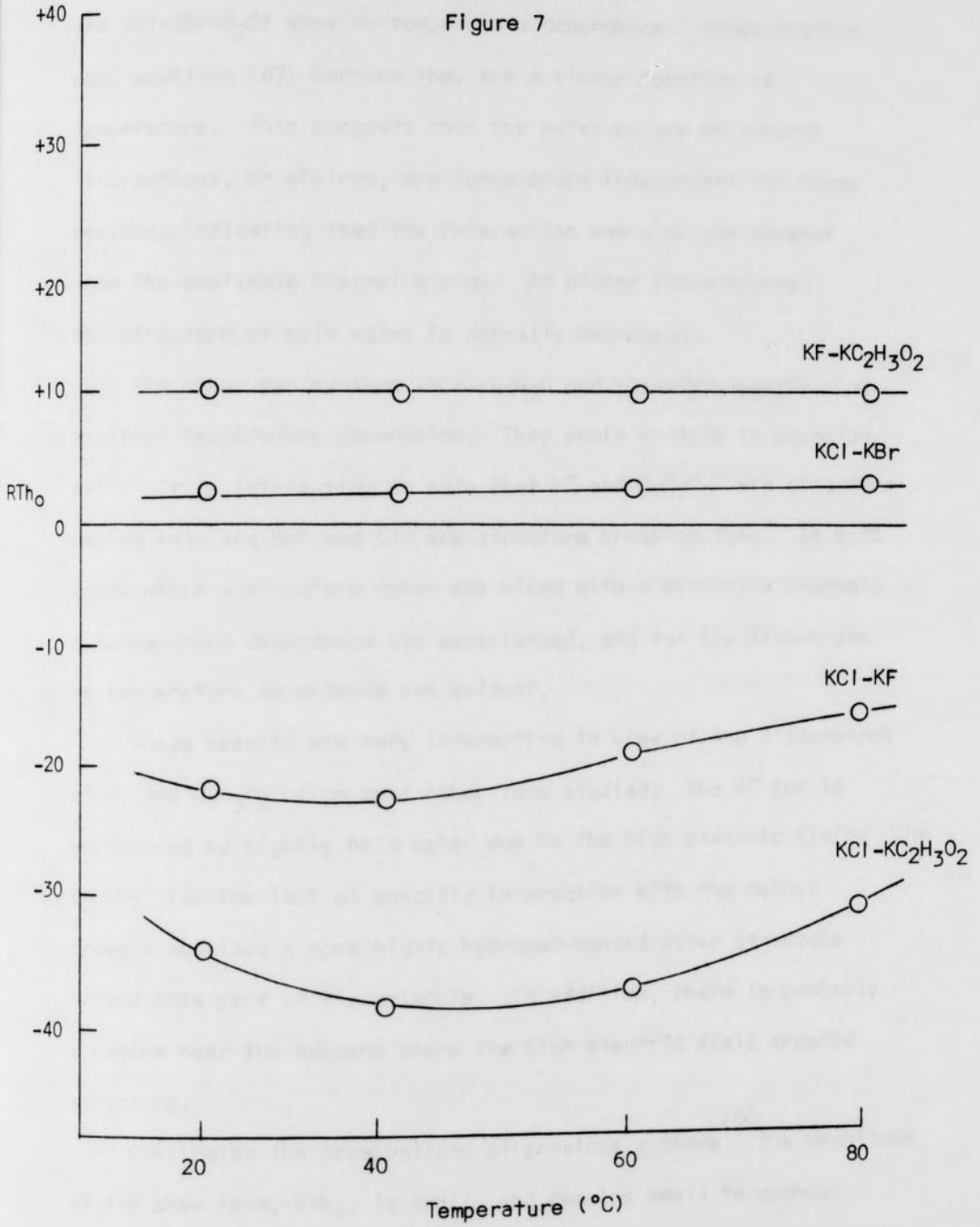
For mixtures which show no temperature dependence for the heats of mixings this equation reduces to:

$$\Delta_m G^E(t_1) = \Delta_m G^E(t_1) - \Delta_m S^E(t_1)\Delta T \qquad \text{(Eq. 87)}$$

As mentioned above, two of these mixtures (KF-$KC_2H_3O_2$-H_2O

RTh_o Versus Temperature

Figure 7



and KCl-KBr-H_2O) show no temperature dependence. These systems obey equation (87) because they are a linear function in temperature. This suggests that the water-solute structural interactions, or mixings, are temperature independent for these systems, indicating that the interaction energies are greater than the available thermal energy. At higher temperatures, the structure of bulk water is normally decreased.

The other two systems (KCl-KF-H_2O and KCl-$KC_2H_3O_2$-H_2O) show a slight temperature dependence. They would conform to equation (85). It is interesting to note that F^- and $C_2H_3O_2^-$ are structure making ions and Br^- and Cl^- are structure breaking ions. In both cases where a structure maker was mixed with a structure breaker, a temperature dependence was experienced, and for the like-types no temperature dependence was evident.

These results are very interesting in view of the differences of F^- and $C_2H_3O_2^-$ from most other ions studied. The F^- ion is surrounded by tightly held water due to the high electric field. The $C_2H_3O_2^-$ ion the lack of specific interaction with the methyl group stabilizes a more highly hydrogen-bonded water structure around this part of the molecule. In addition, there is probably a region near the oxygens where the high electric field creates structure.

Confirming the observations of previous authors[100] the magnitude of the skew term, RTh_1, is small, and remains small throughout the range of temperatures studied in this work. This is postulated as meaning triplet interactions of the types $M^+X^-M^+$ or $M^+Y^-M^+$, or

higher-order interactions do not gain in importance at the higher temperatures. Also postulated by the above authors is that since the heats of mixing do not change dramatically with temperature, one can conclude that whatever the interactions are, they are changing only in degree rather than in kind.

By using the Frank, Evans and Wen model[101] to explain the author's results, validity is added to the premise that the specific interactions observed upon mixing involve ion-solvent interactions in the region of the primary hydration sphere. This region is at the interface between the primary hydration sphere and the disordered water in the structure broken region. Temperature sensitivity of water surrounding ions in solution has been well documented[102], and it has been established that bulk water is reasonably temperature sensitive, while the primary hydration sphere is temperature independent (see Frank, et. al.[66]).

For the systems $KF-KC_2H_3O_2-H_2O$ and $KCl-KBr-H_2O$, the interactions would appear to be at the interface of the primary hydration sphere. Due to the high electrical nature of the F^- and $C_2H_3O_2^-$ ions, the author postulates a less well defined boundary between the region of primary and secondary hydration for these ions (see figure 2), which could have some temperature sensitivity[103, 104] (see for example L. A. Petree[103]). This sensitivity could in turn affect the heats of mixing, making them temperature dependent to a slight degree.

Petree[103] gives a good documentation of the evidence ruling out bulk water interactions as the cause for temperature sensitivity.

Also the lack of stability of the secondary hydration sphere with respect to temperature rules it out as a probable cause.

Desnoyers, et. al.[105], found that two solutes will attract each other if their structural influences are compatible with each other, and incompatible if these structural influences are opposite, leading to repulsion.

This interpretation is derived from the Gurney co-sphere model. The system would apply in the following manner: since the Br^- and Cl^- are of the same structure orienting class, and F^- and $C_2H_3O_2^-$ are heavily hydrated, each of these pairs tend to attract one another. The Cl^-- F^- and Cl^- - $C_2H_3O_2^-$ interactions are of different orienting influences, and repulsion occurs. The Gurney model predicts a positive H^{Ex} for the F^- - $C_2H_3O_2^-$ mixture and Cl^- - Br^- mixtures. Both Cl^- - F^- and Cl^- - $C_2H_3O_2^-$ are predicted to have a negative H^{Ex}.

THERMODYNAMICS

In any work of this nature, a secondary benefit is the calculation of related thermodynamic functions. As seen in equation (85) the excess free energy and excess entropy variations with temperature can easily be calculated provided some reference excess free energy is available. The excess free energy of the component single electrolyte solutions are obtainable from activity and osmotic coefficients. This data is readily available at 25°C. The values are listed in tables 6 and 7. However, data necessary for the calculation of the excess free energy of mixing at a

reference temperature for the systems studied by this author are not available. The usual method of calculation uses data from electromotive force, isopiestic and freezing point lowering experiments. The apparent lack of data has also been observed by Anderson, Wilson and Smith [104].

In table (5) the $\Delta_m H^E$ values along with the RTh_o and RTh_1 values are listed. Also listed in table (8) are the $\Delta C_{p(m)}$ values for equation (86) using the equation:

$$\Delta C_{p(m)} = \frac{\Delta_m H(t_2) - \Delta_m H(t_1)}{\Delta T} \qquad \text{(Eq. 86)}$$

TABLE V

Heats of Mixing

Salt Pair	T	RTh_o	RTh_1	ΔH_m, Y = 0.5
KF-KCl	25°C	-22.6 ± 0.2[a]	-0.8 ± 0.3	-5.65 ± 0.05
	40°C	-23.0 ± 0.3	--	-5.60 ± 0.17
	60°C	-19.9 ± 0.5	+2.0 ± 0.7	-4.97 ± 0.13
	80°C	-16.4 ± 0.8	--	-4.10 ± 0.20
KF-$KC_2H_3O_2$	25°C	+9.5 ± 0.3[a]	+0.9 ± 0.4	+2.38 ± 0.08
	40°C	+9.4 ± 0.4	--	2.35 ± 0.10
	60°C	+10.1 ± 0.6	--	2.52 ± 0.15
	80°C	+10 ± 1	--	2.50 ± 0.25
KCl-KBr	25°C	+3.2[a]	--	+0.80
	40°C	2.9 ± 0.2		0.72 ± 0.05
	60°C	3.2 ± 0.3	--	0.80 ± 0.08
	80°C	3.9 ± 0.3	--	0.98 ± 0.08
KCl-$KC_2H_3O_2$	25°C	-34.3 ± 0.3	+0.9 ± 0.4	-8.58 ± 0.08
	40°C	-38.1 ± 0.4	+2.8 ± 0.6	-9.52 ± 0.10
	60°C	-37.5 ± 0.4	--	-9.38 ± 0.10
	80°C	-31 ± 2	--	-7.75 ± 0.50

[a] see footnote 84.

TABLE VI

Osmotic Coefficients at 25°C*

Molality	KF	KCl	KBr	$KC_2H_3O_2$
0.1	0.930	0.927	0.928	0.943
0.2	0.919	0.913	0.916	0.944
0.3	0.915	0.906	0.910	0.951
0.4	0.914	0.902	0.906	0.958
0.5	0.915	0.899	0.904	0.968
0.6	0.916	0.898	0.904	0.977
0.7	0.919	0.897	0.904	0.987
0.8	0.923	0.897	0.905	0.997
0.9	0.926	0.897	0.906	1.007
1.0	0.931	0.897	0.907	1.017

* Harned, H.S., and Owen, B.B., The Physical Chemistry of Electrolyte Solutions , Reinhold Publishing Corp., New York, N.Y., 1943

TABLE VII

Activity Coefficients at 25°C*

Molality	KCl	KBr	$KC_2H_3O_2$	KF
0.1	0.769	0.771	0.796	0.774
0.2	0.717	0.721	0.767	0.727
0.3	0.687	0.692	0.752	0.701
0.5	0.650	0.657	0.751	0.672
0.7	0.626	0.637	0.755	0.657
1.0	0.605	0.617	0.779	0.649

* Harned, H.S., and Owen, B.B., The Physical Chemistry of Electrolyte Solutions, Reinhold Publishing Corp., New York, N.Y., 1943.

TABLE VIII

$\Delta C_{p(m)}$ Values*

Temperature	KCl-KBr	$KCl-KC_2H_3O_2$	KCl-KF	$KF-KC_2H_3O_2$
25°C-40°C	-.005	-.026	-.001	+.063
40°C-60°C	+.004	-.014	+.008	-.008
60°C-80°C	+.001	-.043	-.001	-.801

*Molality $_{(m)}$ = 0.5 for all systems

SUMMARY

The heats of mixing of anions with the major emphasis on temperature dependence was studied for the systems KCl-KF-H_2O, KCl-KBr-H_2O, KCl-$KC_2H_3O_2$-H_2O and KF-$KC_2H_3O_2$-H_2O. Each system was studied at 25°C, 40°C, 60°C and 80°C. In the systems KF-$KC_2H_3O_2$-H_2O and KCl-KBr-H_2O the heats of mixing show no temperature dependence, while the systems KCl-KF-H_2O and KCl-$KC_2H_3O_2$-H_2O shows a small temperature dependence with the RTh_o values going through an apparent minimum at 40° - 50°C.

It is postulated that the interactions among the ions occurs at the interface of the primary hydration sphere. Where a slight temperature dependence occurs, it is postulated that the boundary between the primary and secondary hydration spheres is less well defined.

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APPENDIX

COMPUTER PROGRAM FOR $\Delta_m H^E$

```
      DIMENSION DELH(100),CI(100),CF(100),PHII(100),PHIF(100),FI(100),
               F2(100),F3(100),W(100),HCAIC(100),ERROR(100),CO(100).
      HSTDF(CM)=SLOPE * ((SQRTF(CM)/(1.0+A * SQRTF(CM))) - ((1./(A *
               A * A * CM)) * (1.4+A * SQRTF(CM) - 1/(1+A * SQRTF(CM)) - 2
               * LOG F(1+A * SQRTF(CM))))).


    1 READ.3,N,A,SLOPE,I
    3 FORMAT (25H I5,F10.3,F10.1,I10)
      IF(I) 50,4,5
    4 READ.2,(DELH(K),CI(K),CF(K),W(K),K=1,N)
    2 FORMAT (F10.1,2F10.1,F10.2)
      I=1
    5 SII=0
      SI2=0
      SI3=0
      S22=0
      S23=0
      S33=0
      SWW=0
      SW=0
      IW=0
      DO9.K=1,N
      PHII(K)=HSTDF(CI(K))
      PHIF(K)=HSTDF(CF(K))
      FI(K)=(-PHII(K))+PHIF(K)+DELH(K)
      F2(K)=CI(K)-CF(K)
      F3(K)=CI(K) * SQRTF(CI(K))-CF(K) * SQRTF
           (CF(K))
      SII=SII+FI(K) * FI(k) * W(K)
      SI2=SI2+FI(K) * F2(k) * W(K)
      SI3=SI3+FI(K) * F3(K) * W(K)
      S22=S22+F2(K) * F2(K) * W(K)
      S23=S23+F2(K) * F3(K) & W(K)
      S33=S33+F3(K) * F3(K) * W(K)
      SWW=SWW+W(K) * W(K)
    9 SW=SW+W(K)
  100 DENOM=(S22 * S33)-(S23 * S23)
      B=((SI2 * S33)-(S23 * SI3))/DENOM
      C=((S22 * SI3)-(SI2 * S23))/DENOM
      SEBC=SII-B * SI2-C * SI3
      PUNCH 3,N,A,SLOPE,I
      PUNCH 7,B,C
```

```
  7   FORMAT(4HB=F10.2,4H C=F10.2)
      PUNCH 8,SEBC
  8   FORMAT(21H SUM ERRORS SQUARED=E10.4)
      PUNCH 12,S11,S12,S13,S22,S23,S33,SWW,SW
 12   FORMAT(8E10.3)
      DF=N-1-1
      SYBC=SORTF(SEBC/DF)
      PUNCH 110,SYBC
110   FORMAT(8H SYBC=F10.4)
 25   PUNCH 24
 24   FORMAT(78H CI CF PHII PHIF HCAIC
      DELH ERROR W)
      DO23 K-1,N
      HCAIC(K)=(+PHII(K))-PHIF(K)+B * F2(K)+
        C * F3(K)
      ERROR(K)=DELH(K)-HCAIC(K)
230   PUNCH 22,CI(K),CF(K),PHII(K),PHIF(K),
        HCAIC(K),DELH(K),ERROR(K),W(K)
 22   FORMAT(2F10.7,4F10.3,2F10.4)
 20   BO=S12/S22
      SEB=S11-BO * S12
      DF=N-1-1
      F=(SEB-SEBC) * DF/SEBC
      PUNCH 26,BO
 26   FORMAT(5H BO=F10.2)
      PUNCH 8,SEB
      PUNCH 27,F
 27   FORMAT(13H F(1,N-2)=F12.4)
      SYB=SQRTF(SEB/(DF+1.0)
      PUNCH 111,SYB
111   FORMAT(7H SYB=F10.4)
 28   IF(IW)29,32,30
 29   PRINT 31
 31   FORMAT(5H TILT)
 32   S11=0
      S12=0
      S13=0
      S22=0
      S23=0
      S33=0
      SWW=0
      SW=0
      DO35K=1,N
      S11=S11+F1(K) * F1(K)
      S12=S12+F1(K) * F2(K)
      S12=S13+F1(K) * F3(K)
      S22=S22+F2(K) * F-2(K)
      S23=S23+F2(K) * F3(K)
      S33=S33+F3(K) * F3(K)
      SWW=SWW+1.0
 35   SW=SW+1.0
      IW=1
```

```
      GO TO 100
 50   READ 40,L,A,SLOPE,B,C,M
 40   FORMAT(I10,4F10.5,I10)
 51   READ 47,(CO(J),J=1,L)
 47   FORMAT(F10.6)
200   IF(M) 42,42,41
 41   PAUSE 20000
      GO TO 1
 42   PUNCH 43,A,SLOPE,B,C
 43   FORMAT(4H A=F10.4,10H SLOPE=F10.2,4H
        B=F10.2,4HC=F10.2)
      DO45 J=1,L
      PHI=HSTDF(CO(J))+CO(J) * (B+C *
        SORTF(CO(J)))
      SQ=SORTF(CO(J))
      EL2=(SLOPE * SQ/(1.+A * SQ))+CO(J) *
        (2. * B 2.5 * C * SQ)
 45   PUNCH 46,CO(J),PHI,SQ,EL2
 46   FORMAT(F15.10,F10.2,F15.6,F10.2)
      GO TO 1
      END
```